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Title: Advances in Modeling Coal Pyrolysis, Char Combustion, and Soot Formation from Coal and Biomass Tar

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Advances in Modeling Coal Pyrolysis, Char Combustion, and Soot Formation from Coal and Biomass Tar

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Motivation: Improved Simulations of Coal Boilers

- We think we know a lot about
  - ✓ Coal pyrolysis
  - ✓ Char oxidation
  - ✓ Ash transformation & deposition
  - ✓ Soot formation
  - ✓ Radiative heat transfer
  - ✓ NO_x and SO_x formation
  - ✓ Turbulence
  - ✓ Turbulence-chemistry interactions
- Do we really know all of this information?
- What else is there to know?

Outline

1. Volatiles Composition
2. Soot formation
3. Char Oxidation

Approaches to Gas-Phase Chemistry in Boiler Simulations

- Coal gas mixture fraction
  - 2 coal gas mixture fractions
- Eddy dissipation
  - Simple chemistry
  - Checks for mixing-limited reaction
- Assume pyrolysis gas species
  - Ignore turbulence?
  - Large eddy simulations?
  - Direct numerical simulations?
  - Combine with GRI-Mech or another large mechanism?

Coal Gas Mixture Fraction

- Assumes all gases from coal have the same elemental composition
  - Char has same elemental composition as pyrolysis gases
- Local chemical equilibrium in gas phase
- Generally used with PDF based on turbulent mixing

- Smith, P. J.; Thomas H, F.; Smoot, L. D., Model for pulverized coal-fired reactors. Symposium (International) on Combustion 1981, 18, (1), 1285-1293.
- Brewster, B. S.; Baxter, L. L.; Smoot, L. D., Treatment of coal devolatilization in comprehensive combustion modeling. Energy & Fuels 1988, 2, (4), 362-370.
- Zhou, M.-m.; Parra-Álvarez, J. C.; Smith, P. J.; Isaac, B. J.; Thornock, J. N.; Wang, Y.; Smith, S. T., Large-eddy simulation of ash deposition in a large-scale laboratory furnace. Proceedings of the Combustion Institute 2019, 37, (4), 4409-4418.

Two Coal Gas Mixture Fractions

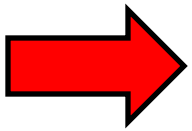
- One mixture fraction for volatiles
- One mixture fraction for elements from char
- Each mixture fraction requires an elemental composition
  - Char assumed to be pure carbon
  - No distinction made for light gases vs. tar
- Local chemical equilibrium in gas phase
- Generally used with PDF based on turbulent mixing

- Flores, D. V.; Fletcher, T. H., The use of two mixture fractions to treat coal combustion products in turbulent pulverized-coal flames. Combustion Science and Technology 2000, 150, (1-6), 1-26.

Species Assumed for Light Gas and Tar

- Light gas:
  - CH_4
- Tar:
  - Ben[illegible] (C_6H_6)
  - A[illegible]ene (C_2H_2)
  - [illegible]ene ($C_6H_5CH_3$)

These are BAD assumptions



- Use detailed gas reaction mechanism, such as GRI-Mech
- Best used in laminar flow

Light Gas during Flash Pyrolysis (Xu & Tomita, Fuel, 1987)

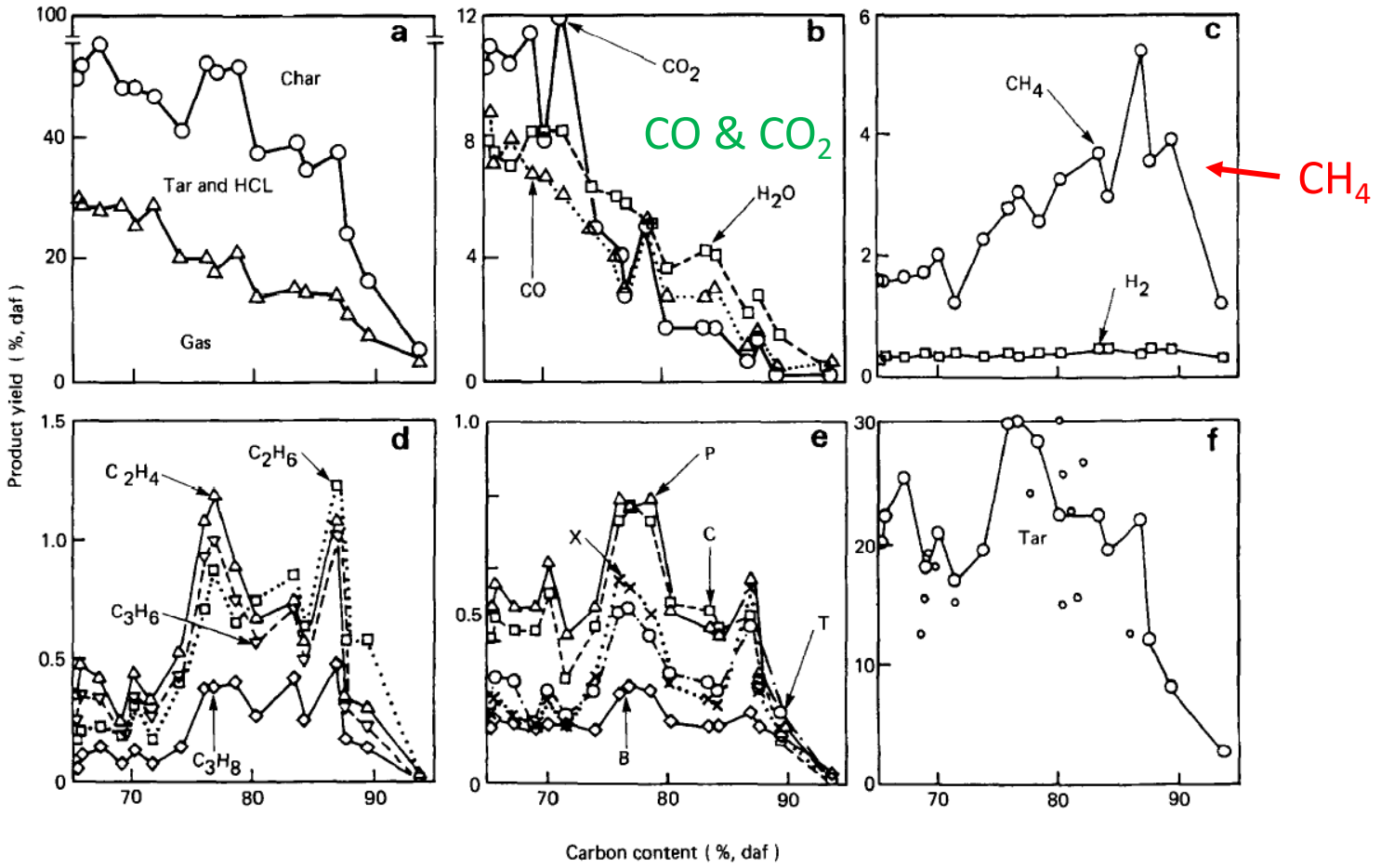


Figure 1 Effect of coal rank on yields of various products. (a) Gas including water, (tar + HCL) and char. (b) Oxygen-containing gases. (c) Methane and hydrogen. (d) C2–C3 hydrocarbons. (e) Hydrocarbon liquids: B, benzene; T, toluene; X, xylene; P, phenol; C, cresol. (f) Tar: ○, Present values; ○, Literature values

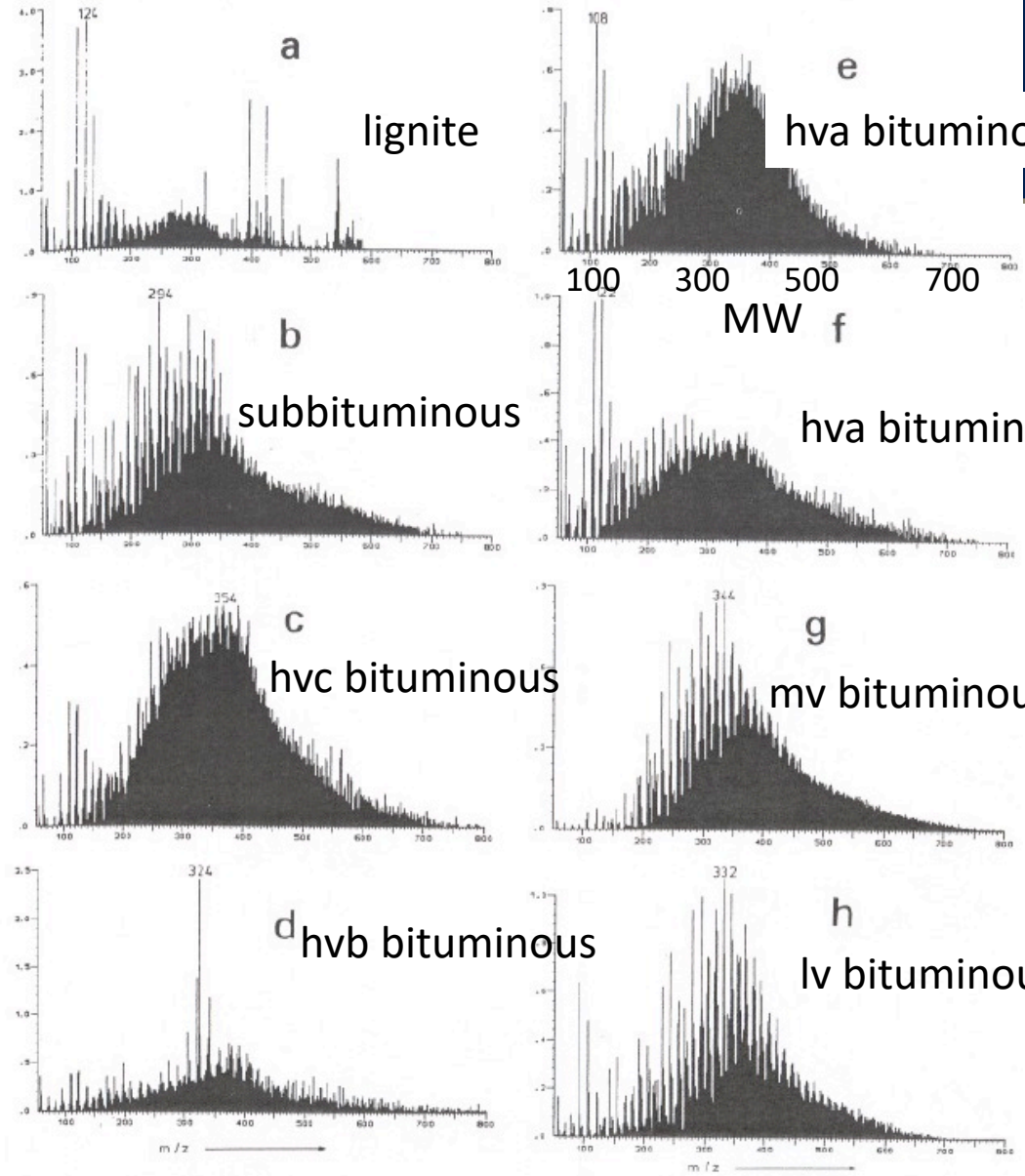


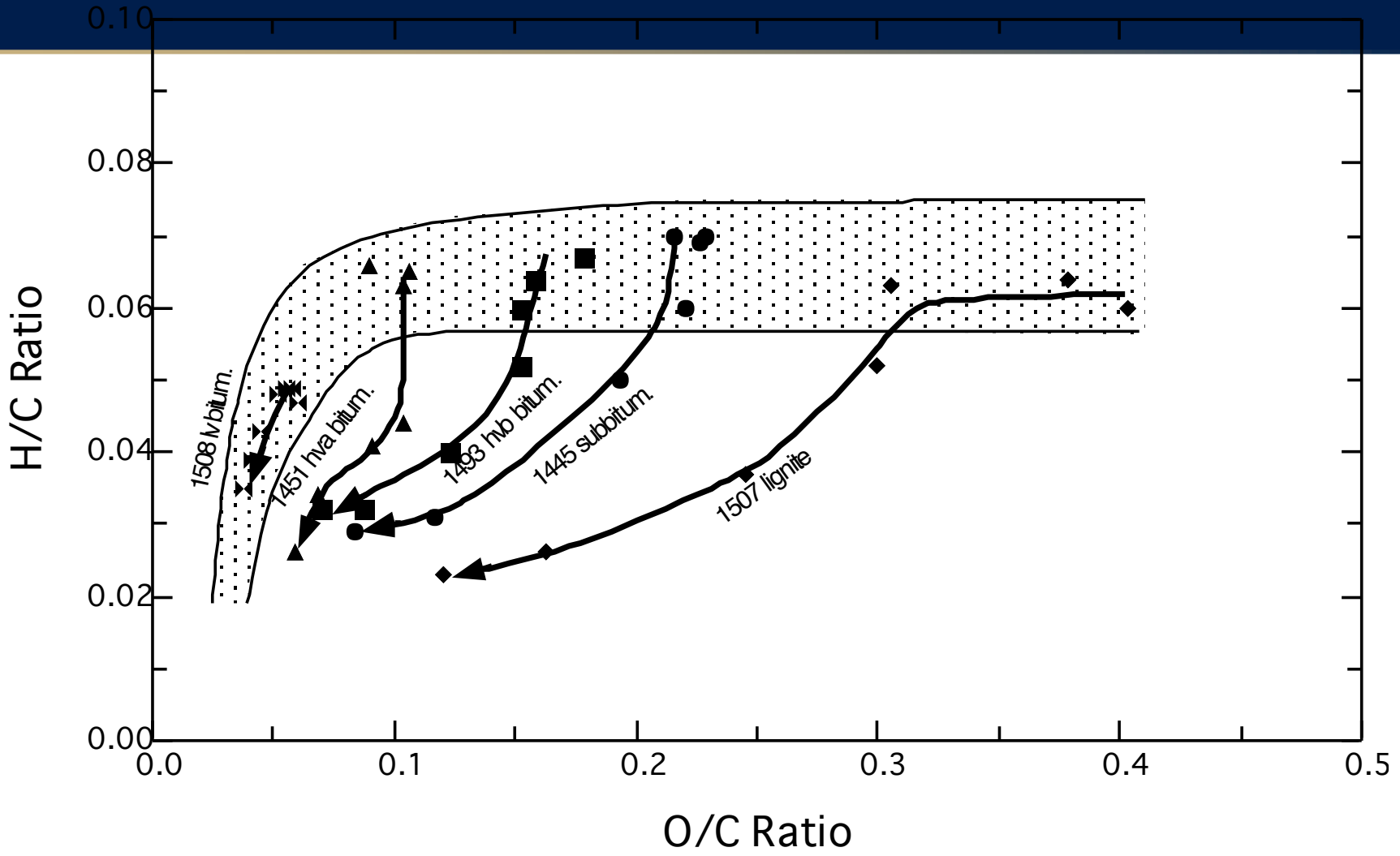
Figure 28. Integrated py-FI mass spectra (50–750°C) of Beulah–Zap (a, $\bar{M}_n$ = 292), Wyodak (b, $\bar{M}_n$ = 338), Illinois #6 (c, $\bar{M}_n$ = 368), Blind Canyon (*d*, $\bar{M}_n$ = 336), Lewiston–Stockton (*e*, $\bar{M}_n$ = 327), Pittsburgh (f, $\bar{M}_n$ = 324), Upper Fremont (g, $\bar{M}_n$ = 368), and Pocahontas #3 (h, $\bar{M}_n$ = 359). Heating rate 100 K/m (Simmleit *et al.*, 1992).

Py-FIMS

- FIMS of tars from the 8 Argonne Premium coal samples
  - Lignite to lv bituminous
- Similar profiles of the “dark” area where most of the mass occurs
- Average MW of tar is ~350 amu
- Tails reach 800 amu

Simmleit et al., in Advances in Coal Spectroscopy, Plenum, New York, pp. 295-339 (1992)

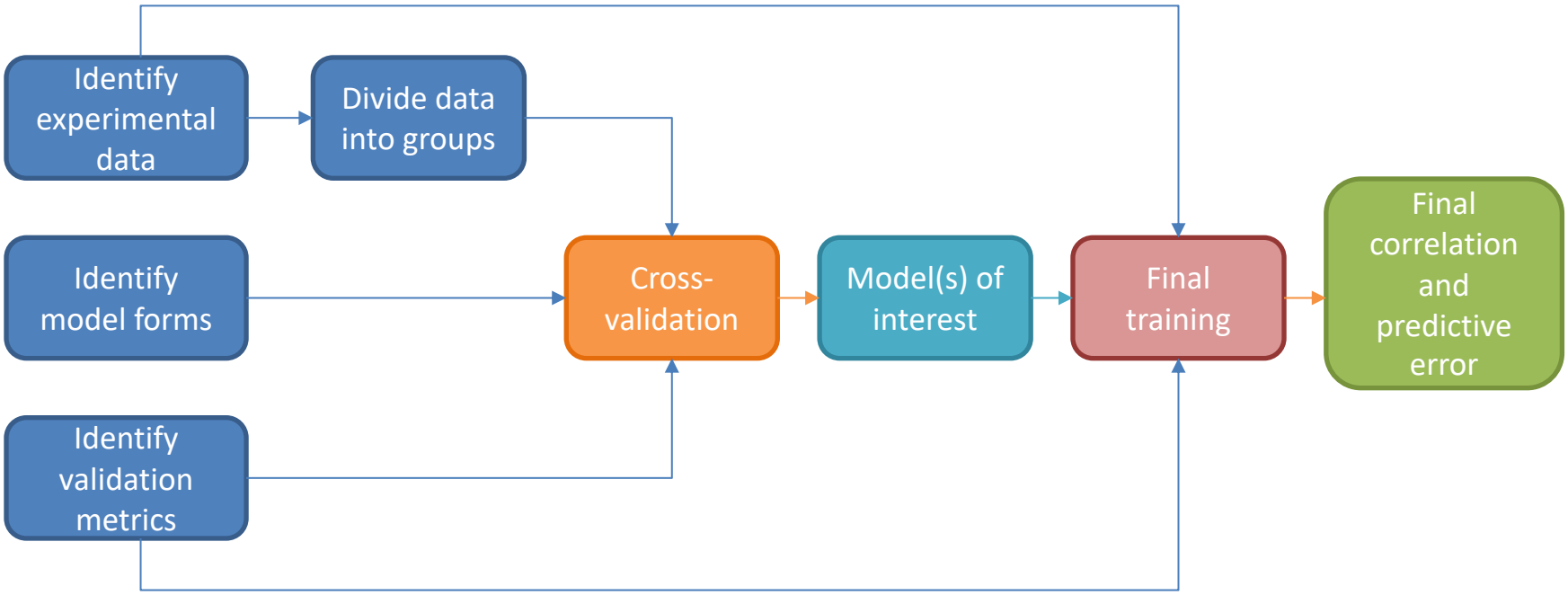
Changes in Char during Pyrolysis



Correlation of Elemental Composition of Coal Tars and Chars

- Gathered sets of composition data that included:
  - Maximum temperature
  - Heating rate
  - Residence time
  - Parent coal composition
    - Ultimate analysis (Elemental composition)
    - Proximate analysis (volatiles, moisture, ash)
- Correlated vs. combinations of the above parameters, plus:
  - Chemical structure parameters (from ^{13}C NMR or NMR correlation)
- Total of 172 model forms attempted for correlation

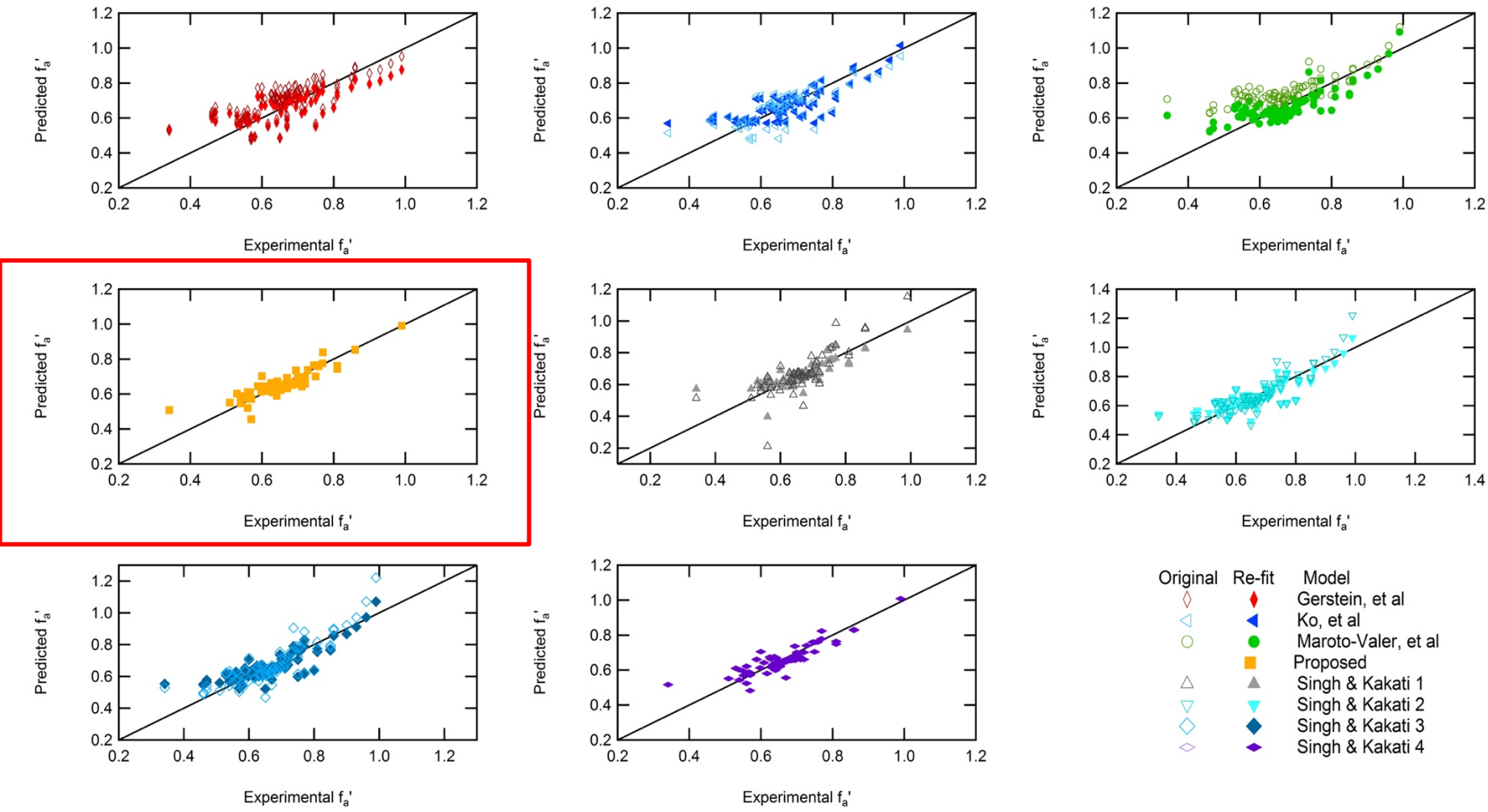
Cross-Validation Process



Cross validation:

1. Divide data into 10 separate groups
2. Use 9 of 10 groups to fit data
3. Use the unused group for independent evaluation
4. Repeat steps 2 & 3, rotating which is the independent group

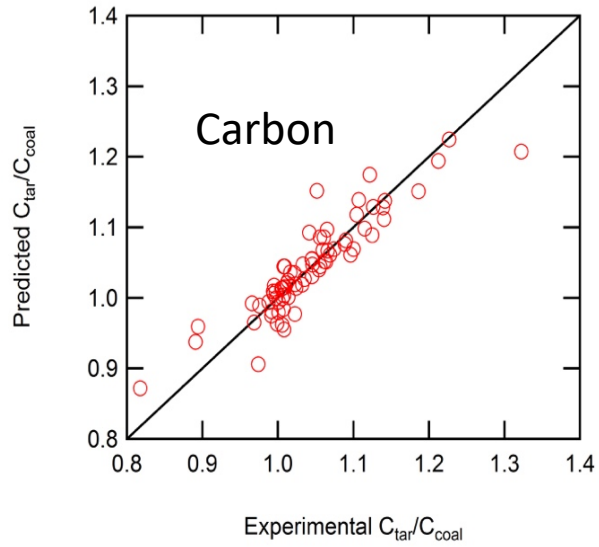
Aromaticity Correlation

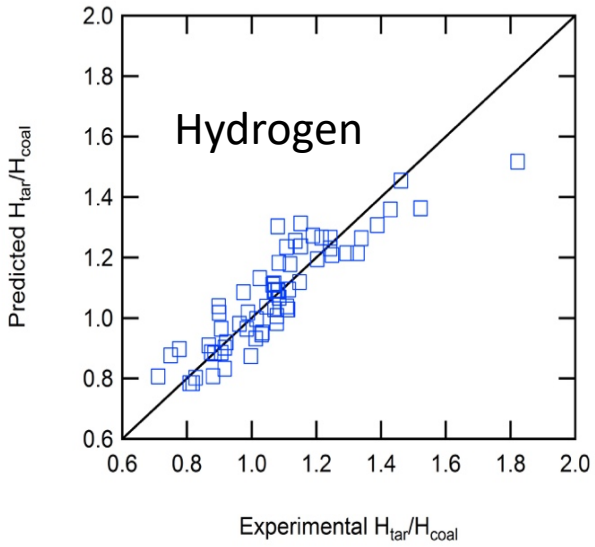


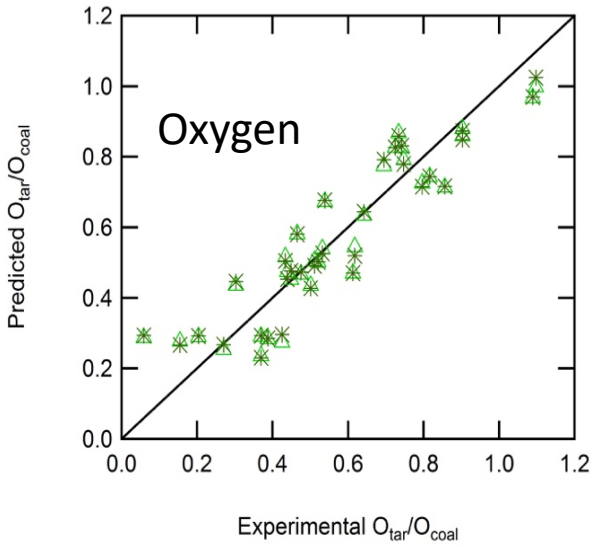
Best Coal Aromaticity Correlation

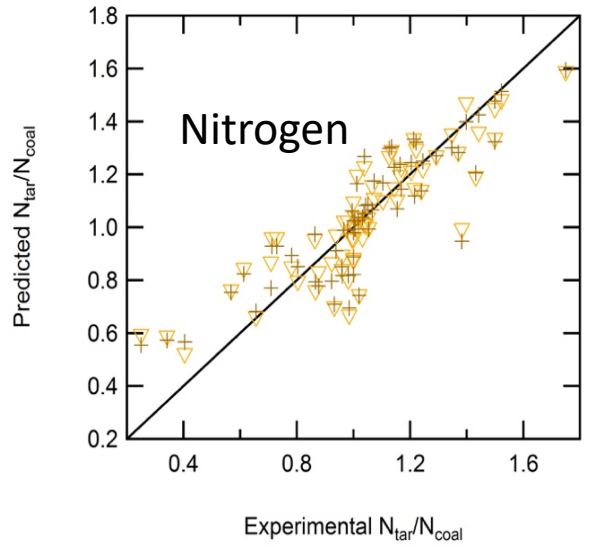
$$f_a' = c_1 + c_2 C_{coal} + c_3 C_{coal}^2 + c_4 H_{coal} + c_5 H_{coal}^2 + c_6 O_{coal} + c_7 O_{coal}^2 + c_8 V_{ASTM} + c_9 V_{ASTM}^2$$

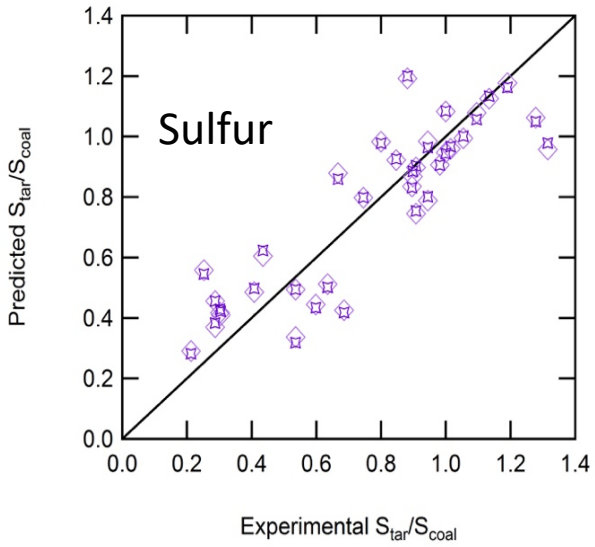
Tar Correlations

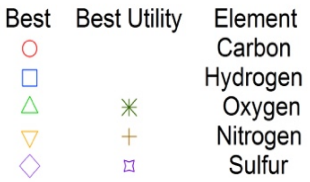












Tar Correlations
(C & H in tar)

$$\frac{C_{tar}}{C_{coal}} = c_1 + c_2 T_{gas,max} + \frac{1}{c_3 T_{gas,max}^3 + c_4 T_{gas,max}^4} + c_5 t_{res} + \frac{1}{c_6 t_{res}^2 + c_7 t_{res}^4} + \frac{1}{1 + c_8 V_{norm}^3} + c_9 C_{coal} + \frac{1}{c_{10} C_{coal}^2 + c_{11} C_{coal}^4}$$

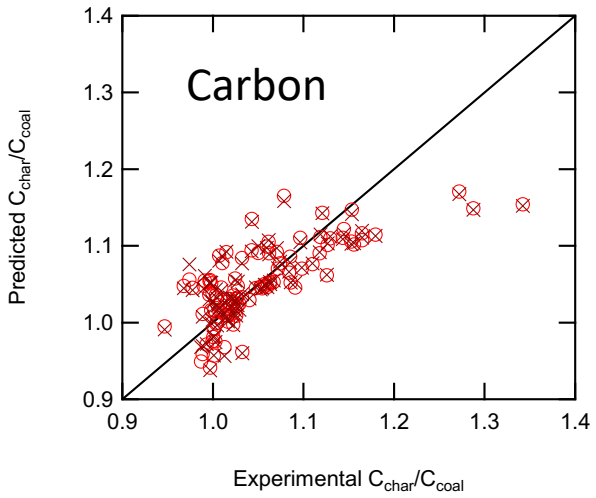
$$\frac{H_{tar}}{H_{coal}} = c_1 + c_2 T_{gas,max} + c_3 t_{res} + c_4 t_{res}^2 + c_5 t_{res}^3 + c_6 V_{norm} + c_7 V_{norm}^2 + c_8 V_{norm}^3 + c_9 M_{\delta,Genetti} + c_{10} M_{\delta,Genetti}^2$$

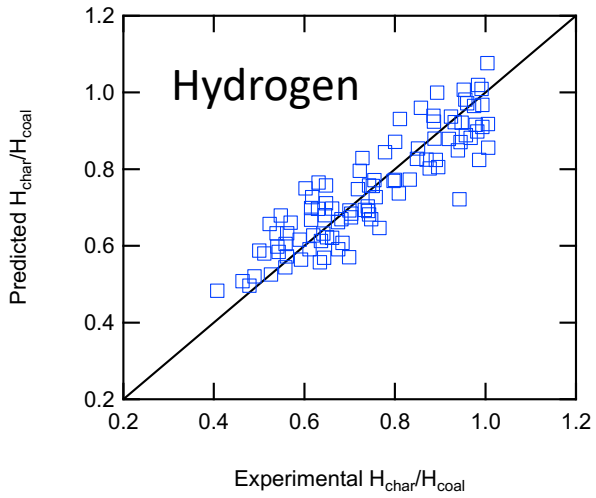
Where

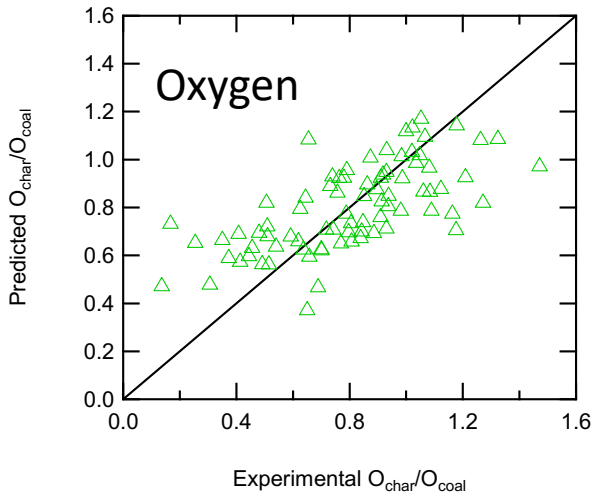
$V_{norm} = V_{meas}/V_{\infty}$

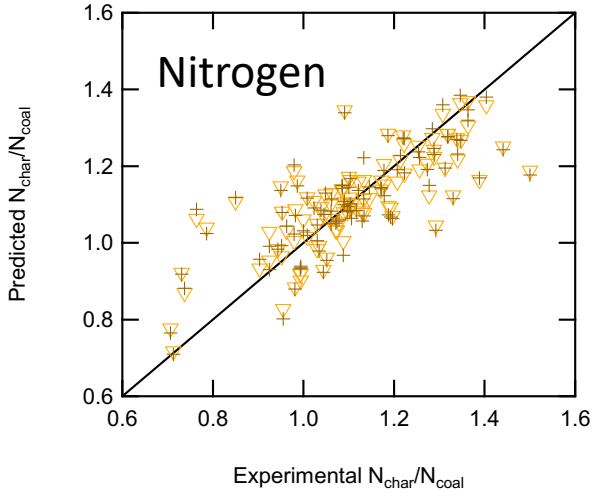
$M_{\delta,Genetti}$ = MW of a side chain in the parent coal, from NMR correlation

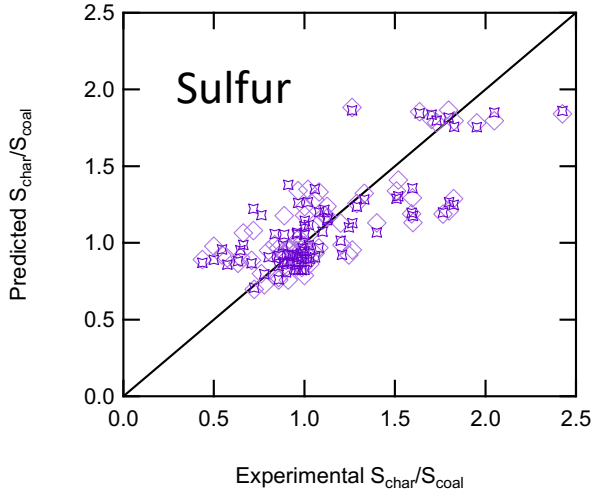
Correlation of Coal Char

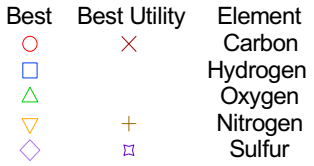












Char Correlations
(C & H in tar)

$$\frac{C_{char}}{C_{coal}} = c_1 + c_2 T_{gas,max} + c_3 T_{gas,max}^{\frac{1}{2}} + c_4 T_{gas,max}^{\frac{1}{4}} + c_5 t_{res} + c_6 t_{res}^{\frac{1}{2}} + c_7 t_{res}^{\frac{1}{3}} + c_8 t_{res}^{\frac{1}{4}} + c_9 \exp(V_{norm}) + c_{10} C_{coal} + c_{11} C_{coal}^{\frac{1}{2}}$$

$$\frac{H_{char}}{H_{coal}} = c_1 + c_2 T_{gas,max}^{c_3} + c_4 t_{res}^{c_5} + c_6 V_{norm}^{c_7} + c_8 H_{coal}^{c_9} + c_{10} V_{ASTM}^{c_{11}}$$

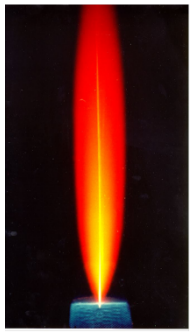
Application to Simulations

1. Estimate heating rate and gas temperature conditions
2. Select coal type and get coal composition data
3. Use correlations to get elemental composition of tar & char
   - gas composition by difference
4. Estimate heat of formation for tar, char, & gas
5. Use with equilibrium code & assumed shape PDF method
   - Possible to have 3 coal gas mixture fractions?
   - Compatible with soot model?

Outline

1. Volatiles Composition
2. Soot formation
3. Char Oxidation

Why Soot?



- Particles heavily impact radiative heat transfer
- Changes near-burner flame temperature and hence chemistry
- Health and environmental impacts

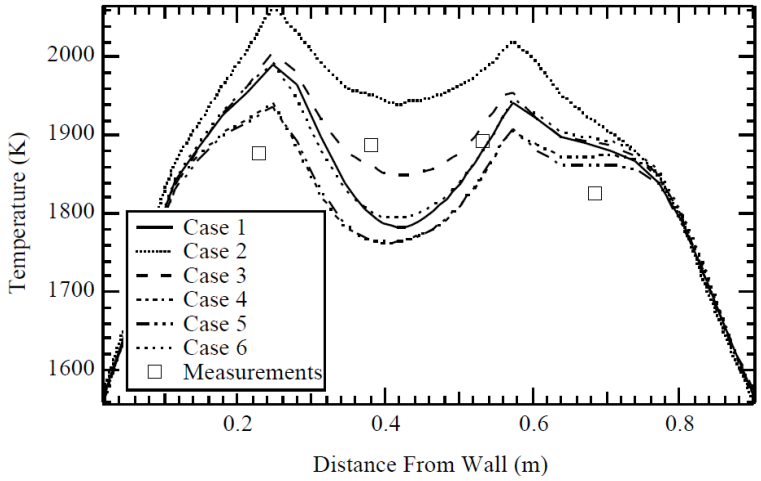
Gaseous Fuels

- Hydrocarbons form acetylene-like radicals
- Acetylene radicals form benzene, PAHs
- Soot precursors are PAHs

Solid Fuels

- Coal gives off tar during primary pyrolysis
- Tar is primary soot precursor
- Only small influence of acetylene mechanism

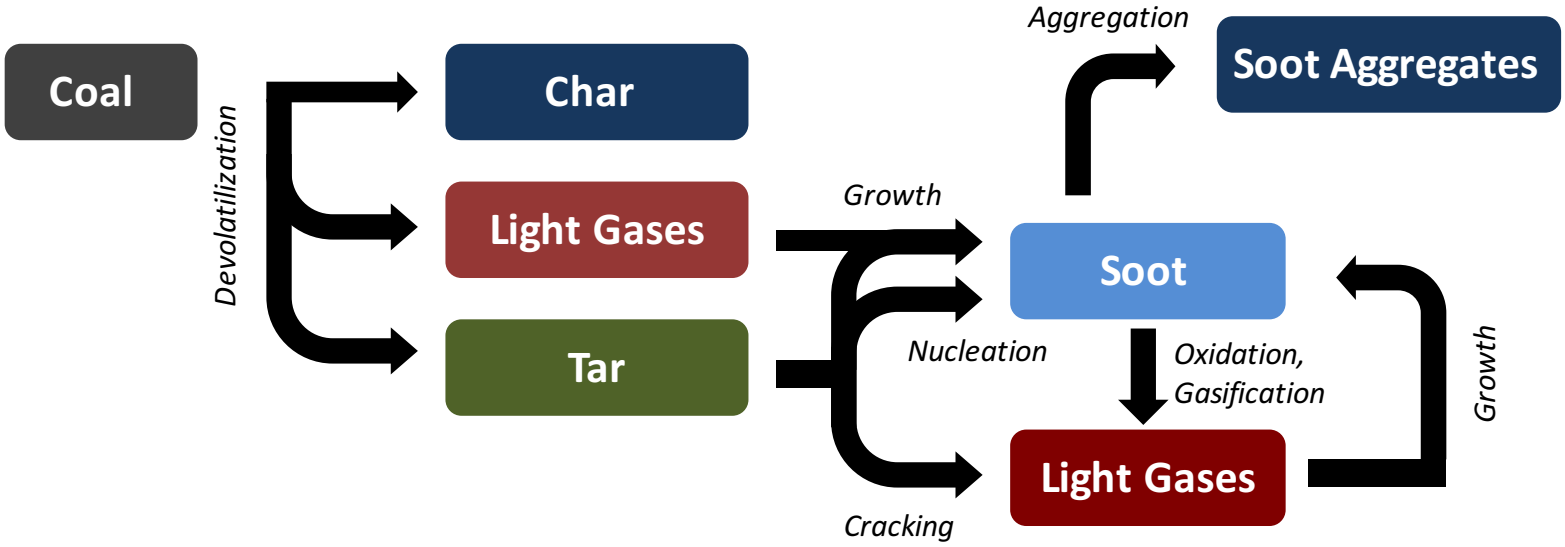
Previous Soot Model
(Brown & Fletcher, E&F 1998)



Predicted and measured gas temperatures in the FPTF at 144.8 cm above the inlet.
(from Brown, 1997)

- CPD model to predict tar yield
- Empirical model for
  tar $\rightarrow$ soot
- Soot growth and oxidation modeled
- Near burner flame temperature decreased by 300 K when soot was modeled

Detailed soot model
(Josephson & Lignell, 2018)

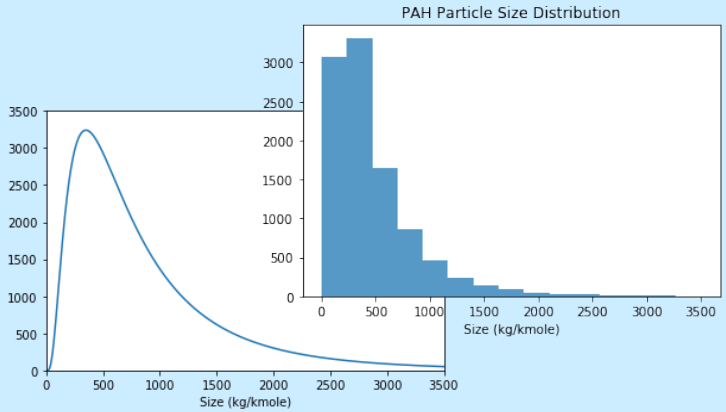


- **Key aspect: formation from tar**
- Tar acts as a nucleation source, and is “closer” to soot
- **Tar** *formed* from coal devolatilization
  - *Consumed* by oxidation, gasification, cracking, deposition, soot nucleation
- **Soot** *formed* from **tar** nucleation, deposition, **light gas** nucleation, growth
  - *Consumed* by oxidation, gasification, (coagulation, aggregation)

Detailed soot model

Precursors

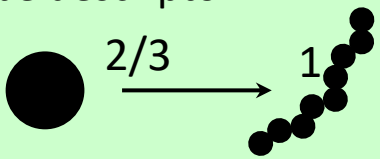
- Sectional model
- Transport 9 sections (5 in Arches)
- Fixed bins
- CPD model output
  - tar yield
  - MW distribution
- Coagulation (FM) → soot



Soot

- MOMIC (moment method)
- Transport 6 moments (5 in Arches)
- Aggregation as in *Balthasar & Frenklach (2005)*
  - $M_{<d>}$ transported
  - Defines a shape descriptor

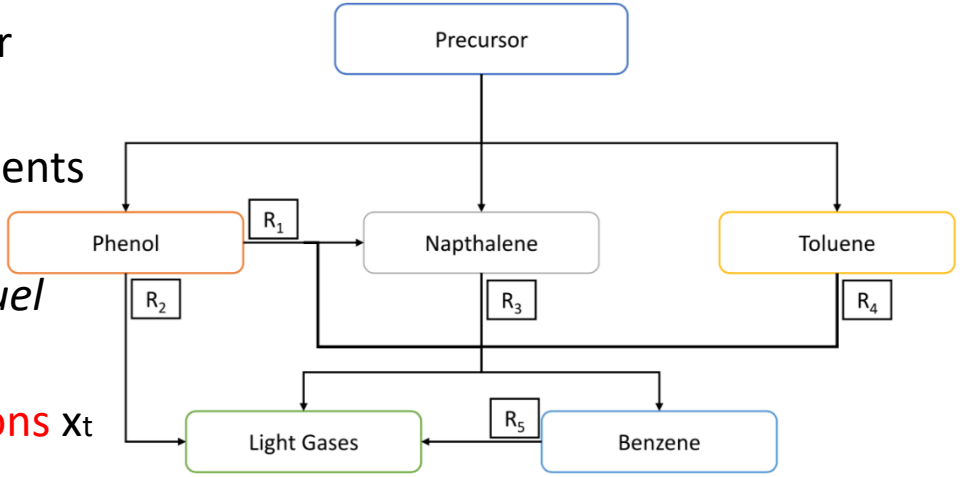
$$\langle d \rangle = \frac{\log \mu_{\langle d \rangle}}{\log \mu_1}$$



- Tar nucleation
- Tar deposition (collisional growth)
- HACA growth (C_2H_2)
- O_2+OH oxidation
- CO_2+H_2O gasification

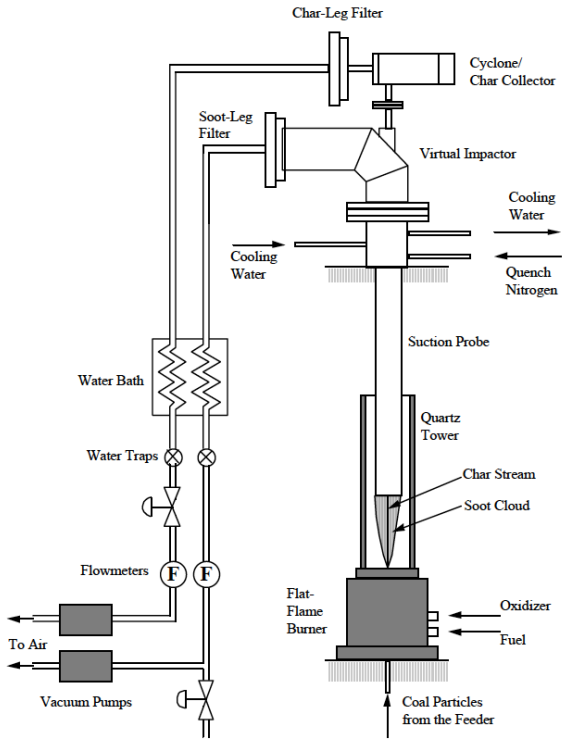
Tar cracking model

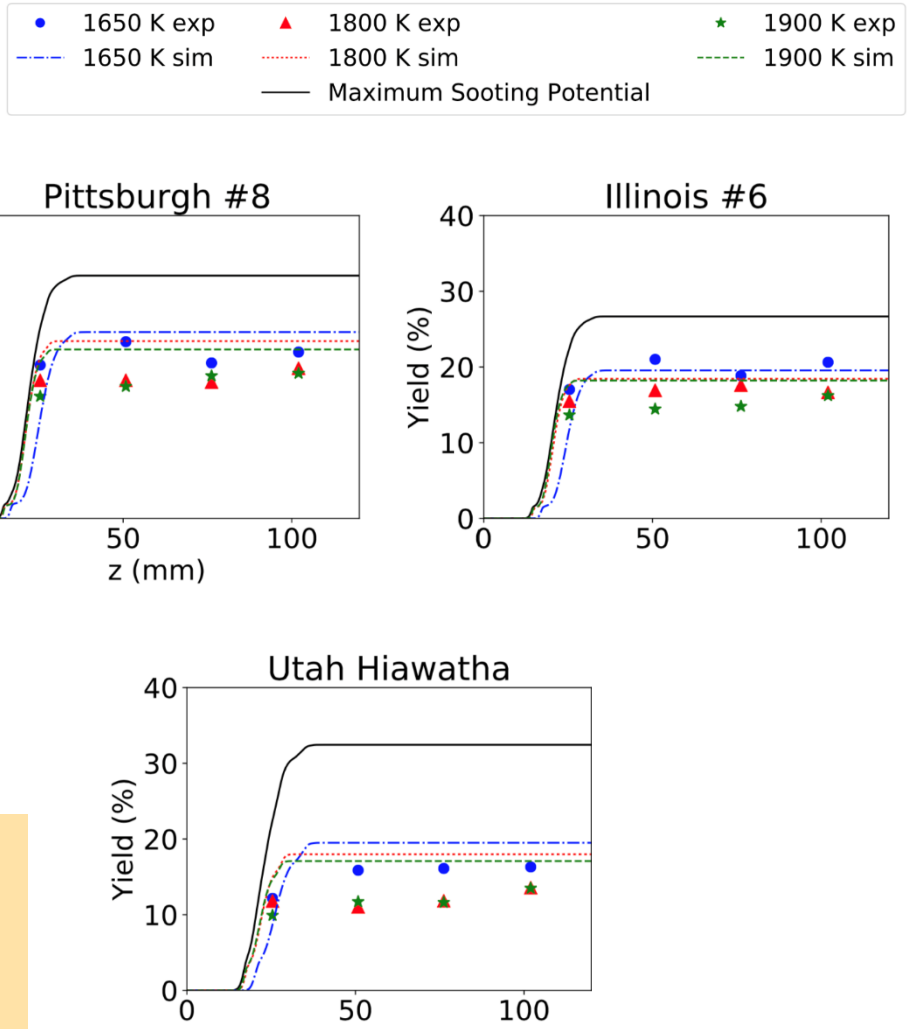
- Tar cracking mechanism is important for accurate modeling.
- Tar molecules include aliphatic components and heteroatoms
- Model based on that by *Marias et al. Fuel Process. Technol. 149:139-152 (2016).*
- Tars taken as consisting of 4 type fractions x_t as a surrogate:
  - Phenol, toluene, naphthalene, benzene
- Components react to others, or to gas phase
- Rates for each tar section are computed from x_t, reaction rates, and fraction of MW cracked to gas
- Type fractions x_t taken as constant, precomputed for each fuel type/system



Reaction	Rates
$C_6H_6O \longrightarrow CO + 0.4C_{10}H_8 + 0.15C_6H_6 + 0.1CH_4 + 0.75H_2$	$R_1 = k_1[C_6H_6O]$ $k_1 = 1.00E7 \exp\left(\frac{-1.0E5}{RT}\right)$
$C_6H_6O + 3H_2O \longrightarrow 2CO + CO_2 + 3CH_4$	$R_2 = k_2[C_6H_6O]$ $k_2 = 1.00E8 \exp\left(\frac{-1.0E5}{RT}\right)$
$C_{10}H_8 + 4H_2O \longrightarrow C_6H_6 + 4CO + 5H_2$	$R_3 = k_3[C_{10}H_8][H_2]^{0.4}$ $k_3 = 1.58E12 \exp\left(\frac{-3.24E5}{RT}\right)$
$C_7H_8 + H_2 \longrightarrow C_6H_6 + CH_4$	$R_4 = k_4[C_7H_8][H_2]^{0.5}$ $k_4 = 1.04E12 \exp\left(\frac{-2.47E5}{RT}\right)$
$C_6H_6 + 5H_2O \longrightarrow 5CO + 6H_2 + Ch_4$	$R_5 = k_5[C_6H_6]$ $k_5 = 4.40E8 \exp\left(\frac{-2.2E5}{RT}\right)$

Validation—Coal

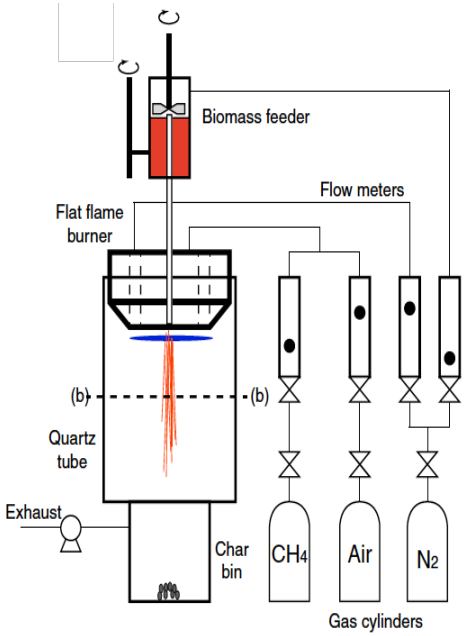


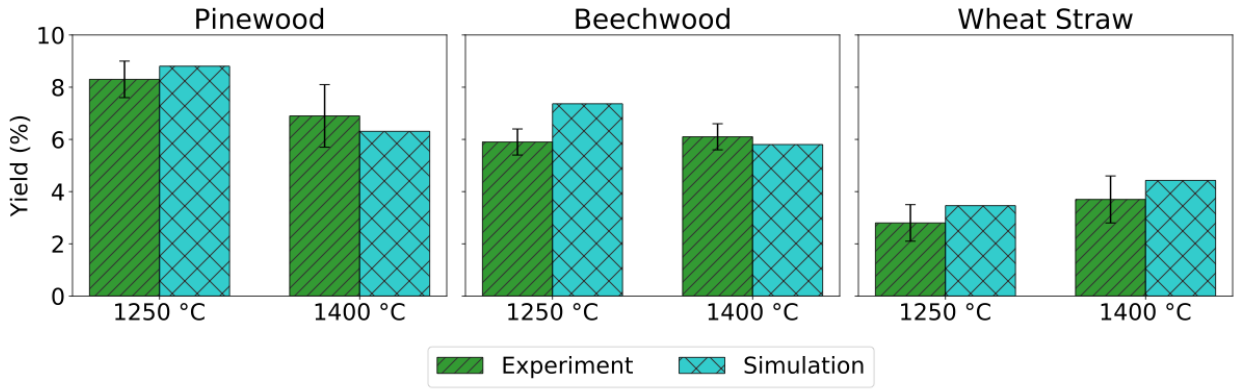


- BYU laminar flat flame burner experiments
- *Ma et al. (1996, 1998)*
- CPD model predicts tar
- Soot model compared with Ma's data

Validation—Biomass (soot yields)

- Trubetskaya et al., Applied Energy, 171, 2016
- Fast pyrolysis drop tube reactor
- Two temperatures: 1250, 1400 °C
- Precursors from CPD-bio



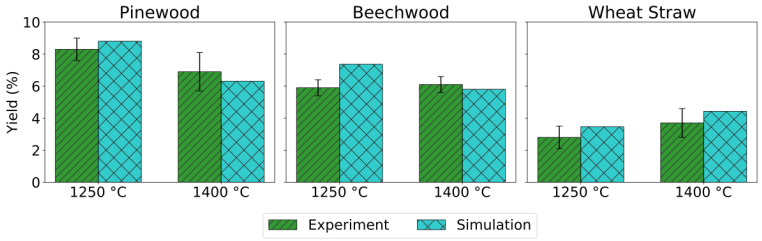


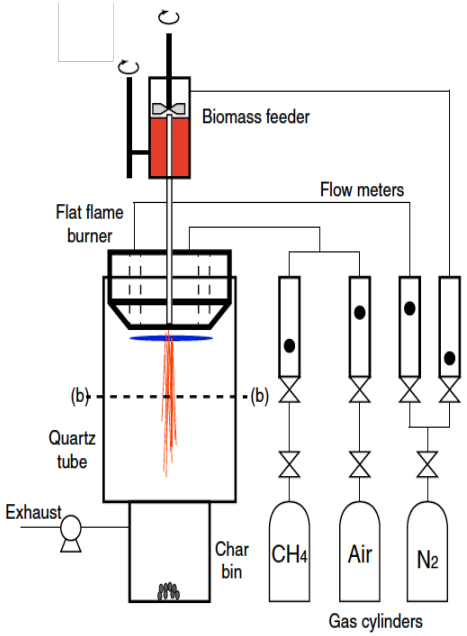
Good agreement with measured soot yield for biomass pyrolysis!
True prediction – no tunable parameters!

Trubetskaya et al., *Applied Energy*, 171, 2016

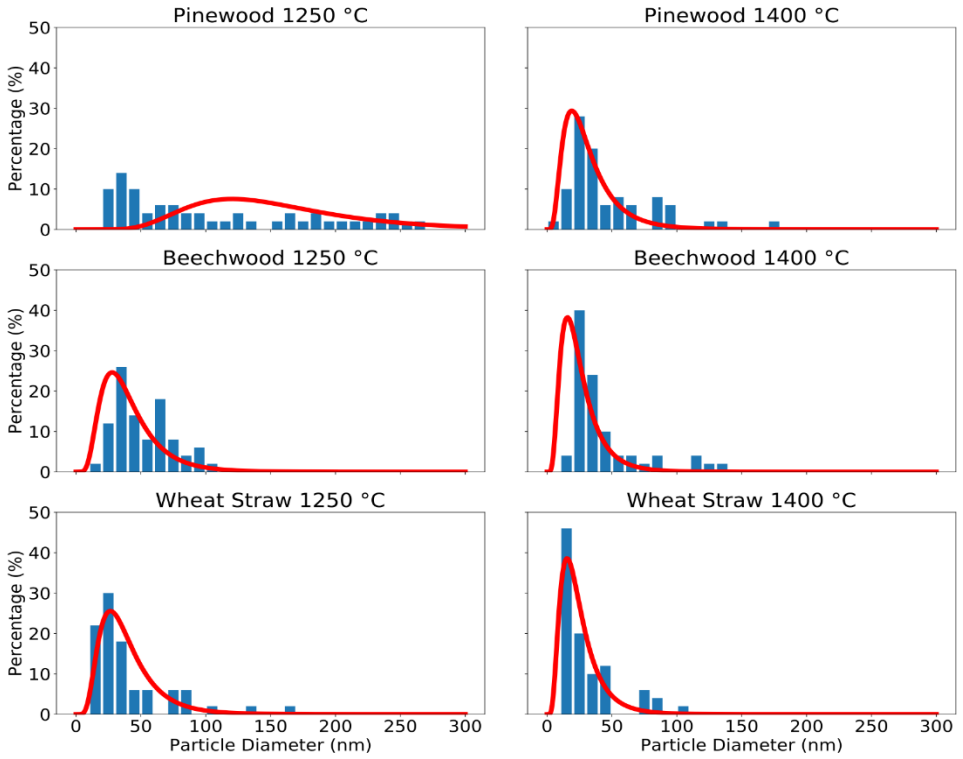
Validation—Biomass (MW distributions)

- Trubetskaya et al., Applied Energy, 171, 2016
- Fast pyrolysis drop tube reactor
- Two temperatures: 1250, 1400 ºC
- Precursors from CPD-bio





Trubetskaya et al., *Applied Energy*, 171, 2016



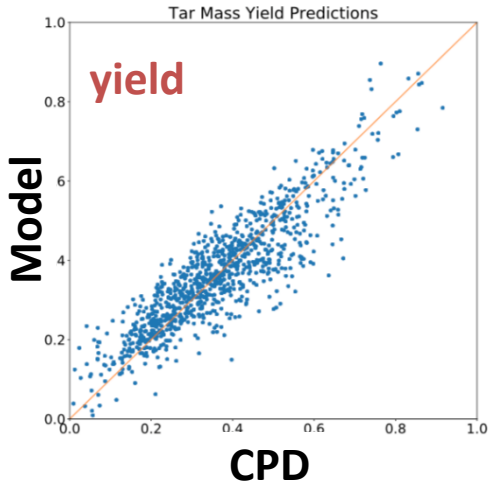
Reasonable agreement with soot size distribution!

Reduced Soot Model

- Detailed model reduced for computational efficiency
  - 5-9 tar sections $\rightarrow$ 1 section
    - Tansport N_t (#/m^3)
  - 5-6 soot moments $\rightarrow$ 2 moments
    - Transport N_s, Y_s
  - Assume spherical particles
    - No “d” moment: $M_{<d>}$
  - Most chemistry is the same
- Correlate tar cracking type fractions x_t
- Sooting potential model

Sooting Potential Model

- CPD run many times varying input parameters
  - T: 800 < T (K) < 3000
  - P: 0.1 < P (atm) < 100,
  - O:C ratio: 0.01 < O:C < 0.35
  - H:C ratio: 0.3 < H:C < 1.1
  - Volatiles: 2 < %Vol < 80
- Correlation: tar yield and tar MW

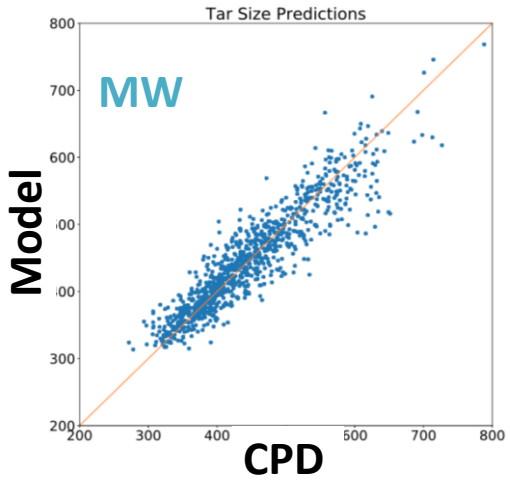


$$y_{tar} = \frac{\begin{array}{r}-124.2 + 35.7P + 93.5O_C - 223.9O_C^2 + 284.8H_C - 107.3H_C^2 \\ + 5.48V + 0.014V^2 - 58.2PC_H - 0.521PV - 5.32H_CV\end{array}}{\begin{array}{r}-303.8 + 52.4P + 1.55E3O_C - 2.46E3O_C^2 + 656.9H_C - 266.3H_C^2 + 15.9V \\ + 0.025V^2 - 90.0PH_C - 462.5O_CH_C + 4.80O_CV - 17.8H_CV\end{array}}$$

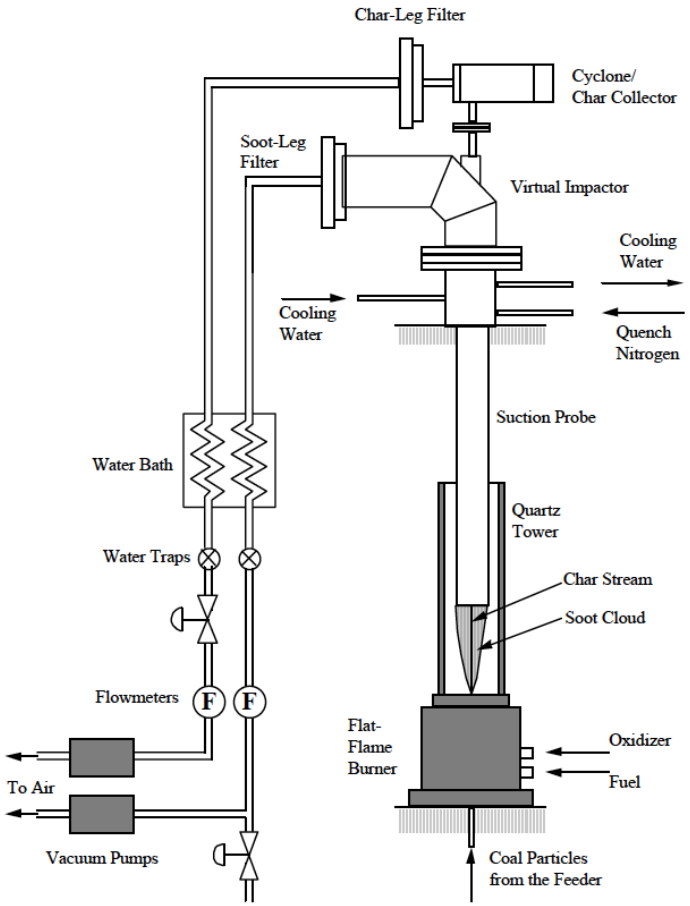
MW

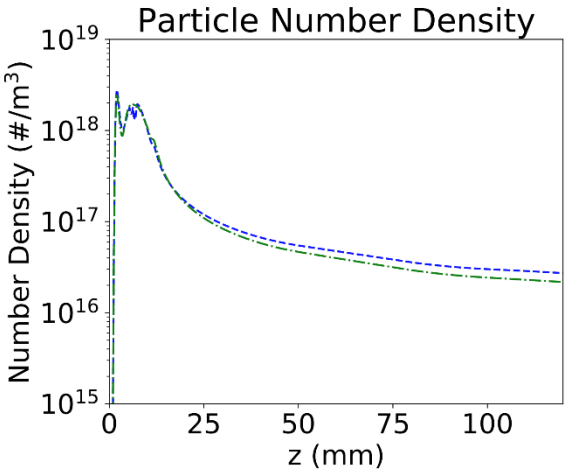
$$m_{tar} = \frac{\begin{array}{r}3.12E5 + 16.4T_g + 4.34E5O_C - 8.48E5H_C + 6.38E5H_C^2 \\ - 361.3V - 0.221T_gV - 6.39E5O_CH_C + 1.91E3H_CV\end{array}}{\begin{array}{r}753.6 + 0.042T_g + 83.9O_C - 1.77E3H_C + 1.20E3H_C^2 + 5.09E\text{-}3T_gP \\ - 0.024T_gH_C - 5.27E\text{-}4T_gV + 0.513PV - 361.0O_CH_C + 3.83H_CV\end{array}}$$

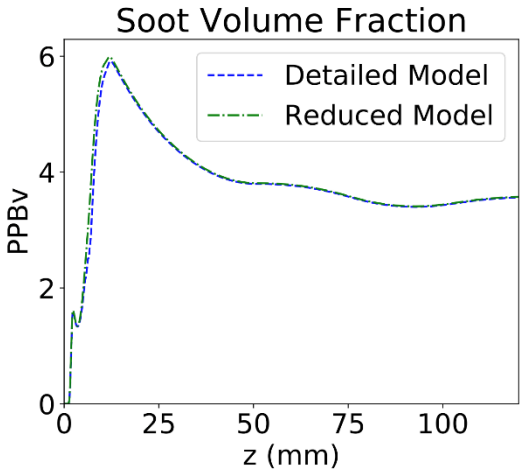
P is log(P)



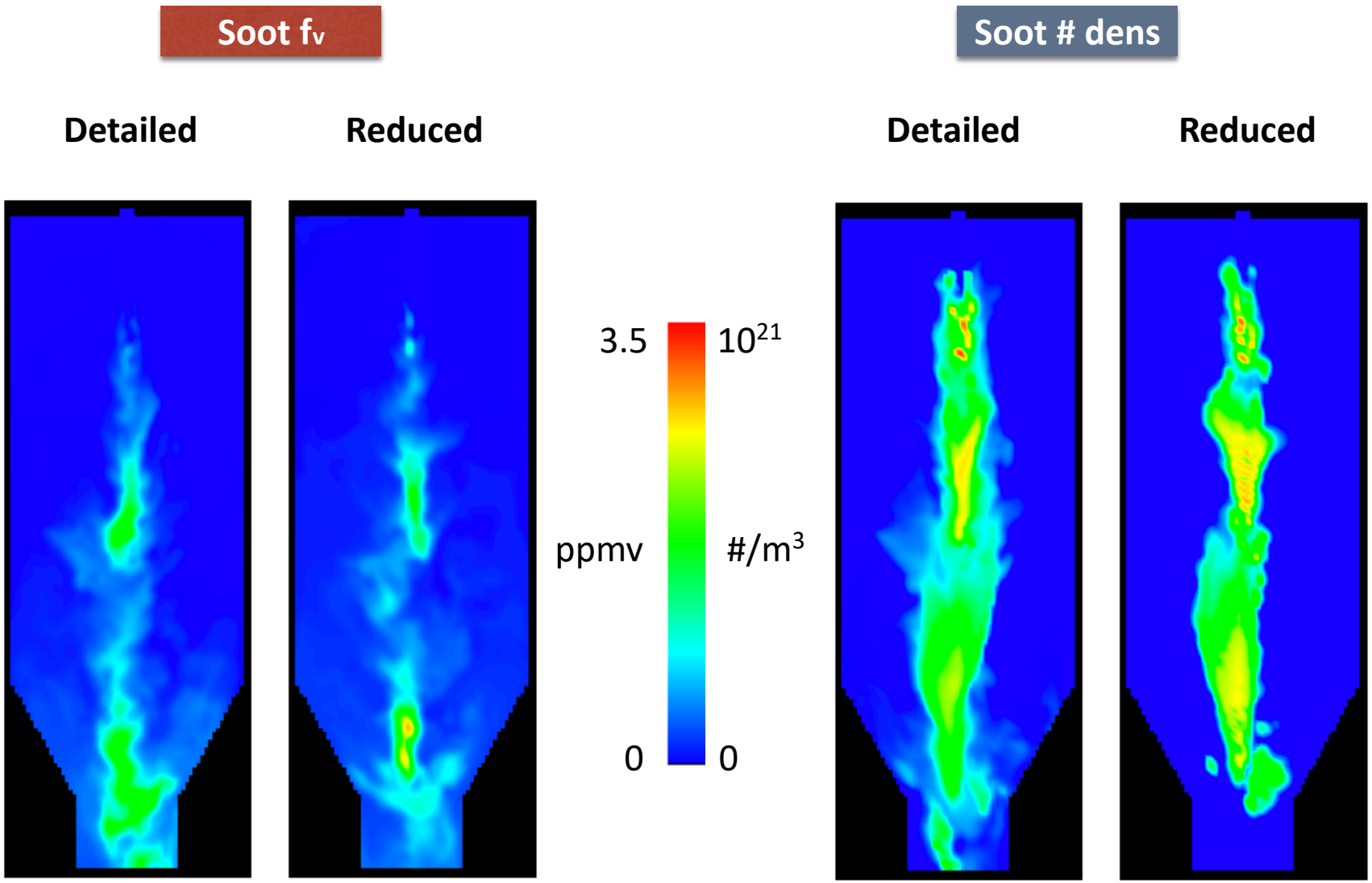
Validation—flat flame burner







Arches simulation—OFC



Outline

1. Volatiles Composition
2. Soot formation
3. Char Oxidation

Wanted:
Coal General Model of Char Oxidation

- Char properties are affected by many factors:
  - Parent coal properties
  - Size
  - Preparation conditions
    - Heating rate
    - Residence time
    - Pressure
    - Peak temperature
    - Oxidizing vs reducing conditions

Comprehensive Char Oxidation/Gasification Models

- CBK (Hurt, et al.)
  - Intrinsic Char-O_2 kinetics
  - Thiele modulus for pore diffusion
  - Swelling model
  - Mode of burning and other parameters
  - Simple annealing model
- CBK-G (Niksa et al.)
  - Similar to CBK, except for gasification by CO_2, H_2O, & H_2
- CCK (Holland & Fletcher)
  - Combined CBK and CBK-G
  - Improved annealing and swelling models

Sensitivity Analysis on CCK for Oxy-fuel Conditions

- Determine which submodels/parameters are most important
  - Not including intrinsic rates
- Global analysis varying all parameters simultaneously testing for both linear and non-linear sensitivity
- 27 parameters, 4 burn-out quartiles, 4 coals, 3 gas conditions, 2 quantities of interest, and 2 types of sensitivity analysis ≈5,000 measures of sensitivity extracted from 120,000 computational experiments

Parameter	Importance
E_A (annealing act. energy)	0.74
n_1 (reaction order)	0.51
d/d_0 (swelling)	0.27
α (mode of burning)*	0.20
d_{grain} (ash grain size)	0.20
σ_{EA} (distribution of E_A)	0.18
t_r (residence time)	0.14

(Holland and Fletcher, 2016)

Possible Solution: Annealing Model (CBK)

$$A_{ox} = f\left[precursor, T_p(t)\right] = A_0 f_{an}$$

Annealing factor

$$\ln(A_0) = 10.96 - 0.07136 * \mathrm{C}$$

$$\frac{dN_i}{dt} = -A_d \exp\left(-E_{d,i}/\left(RT_p\right)\right) N_i$$

Distribution of sites

$$f_{an} = \sum f_i = \sum N_i/N_{i,o}$$

Annealing during Pyrolysis vs Post-pyrolysis

During Pyrolysis

- Coal type
  - Chemical structure
  - Pyrolysis yields
- Heating rate
  - Pyrolysis yields
  - Swelling
  - Pore size
  - Ash distribution
- Peak temperature
  - Pyrolysis yields
  - Ash layer porosity

Post-pyrolysis

- Mode of burning
  - Constant diameter vs constant density
- Residence time
  - Changes in aromatic structure
- Changes with extent of conversion
  - Pore sizes
  - Ash layer
  - Distribution of reactivity
    - Most reactive stuff burns first

Annealing Model: Holland Extension

- The distributed activation energy is bimodal and irregular
- The distribution (not just the reaction rate) depends on
  - coal particle heating rate (*HR*),
  - peak temperature (T_p), and
  - chemical structure (p_0)
- O_2 char conversion may be impacted differently by annealing than CO_2 and H_2O char conversion

Parameter	Value
k_0	$1.398*10^{12}$ s^{-1}
a	0.356 ln(kcal/mol)
b	$3.65*10^{-4}$ ln(kcal/mol)
c	1.531 ln(kcal/mol)
d	0.679 ln(kcal/mol)

$$\frac{df_i}{dt} = -A_d * exp\left(\frac{-E_{A_{anneal},i}}{RT}\right) * f_i$$

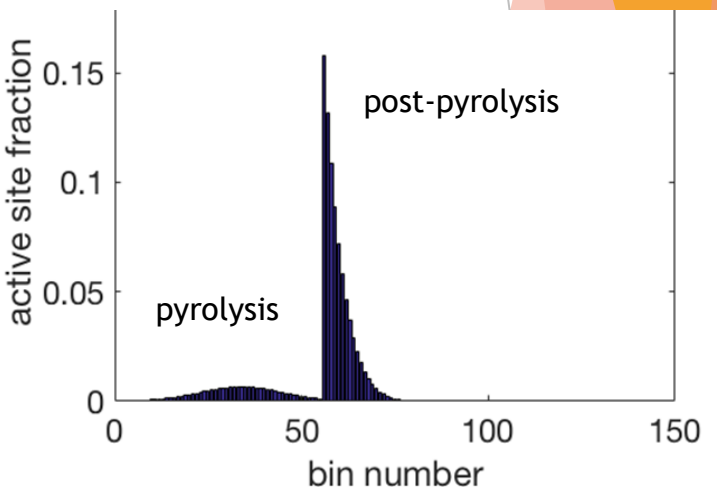
$$PDF(E_{A_{anneal},i}) = \frac{1}{E_{A_{anneal},i}*\sigma} \exp\left(-\frac{1}{2}\left(\frac{ln\left(E_{A_{anneal},i}/\mu\right)}{\sigma}\right)^2\right)$$

$$\mu = a * p_0 + b * T_{peak} + c$$

$$\sigma = \frac{d}{p_0}$$

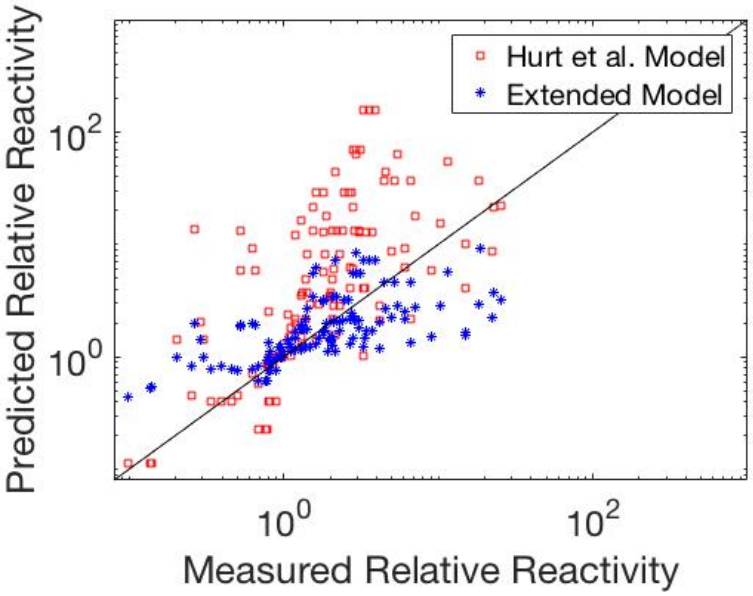
$$A_d = \frac{p_0 * k_0}{\ln(10^4)} \qquad for\ HR \geq 10^4$$

$$A_d = \frac{p_0 * k_0}{\ln(HR + 2.7)} \qquad for\ HR < 10^4$$



Irregular distributed activation energy

Annealing Model: Results by Holland & Fletcher



	Hurt et al. Model			Extended Model		
Model Quantification	**Mean**	**Minimum**	**Maximum**	**Mean**	**Minimum**	**Maximum**
Sum Squared Error	$1.45 \times 10^{5*}$	N/A	N/A	$2.43 \times 10^{3*}$	N/A	N/A
Error Factor: All Points	**6.08**	**1.00**	**51.97**	**2.24**	**1.00**	**9.96**
Error Factor: Least Successful Quartile	17.28	7.00	51.97	4.44	2.30	9.96
Error Factor: Most Successful quartile	1.13	1.00	1.25	1.10	1.00	1.20
Error Factor: Central Quartiles	2.78	1.25	6.50	1.63	1.21	2.27

Error factor reduced from ~6 to ~2 using improved annealing model, including effects of:

- Coal type
- Heating rate
- Peak temperature

Conclusions

- Hope for better chemistry in coal combustion/gasification simulations
  - Correlation for elemental composition of tar & char
  - Not CH_4 and Benzene
- Better treatment of tar leads to improved simulation of soot
  - Generalized soot model
  - Improved local temperature (T_g) predictions
  - Improved T_g will lead to improved NO_x calculations

Conclusions (cont.)

- Hope for coal-general char conversion model
  - Reactivity affected by:
    - Char formation environment
    - Residence time during char conversion
    - Extent of char conversion
  - Annealing model used to treat pyrolysis & post-pyrolysis effects
  - Improved swelling model based on heating rate & coal type
  - Still work to do

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National Nuclear Security Administration

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THE UNIVERSITY OF UTAH

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Berkeley UNIVERSITY OF CALIFORNIA

- Project oversite and guidance is provided from three national labs: Lawrence Livermore, Sandia, and Los Alamos National Laboratories

Lawrence Livermore National Laboratory

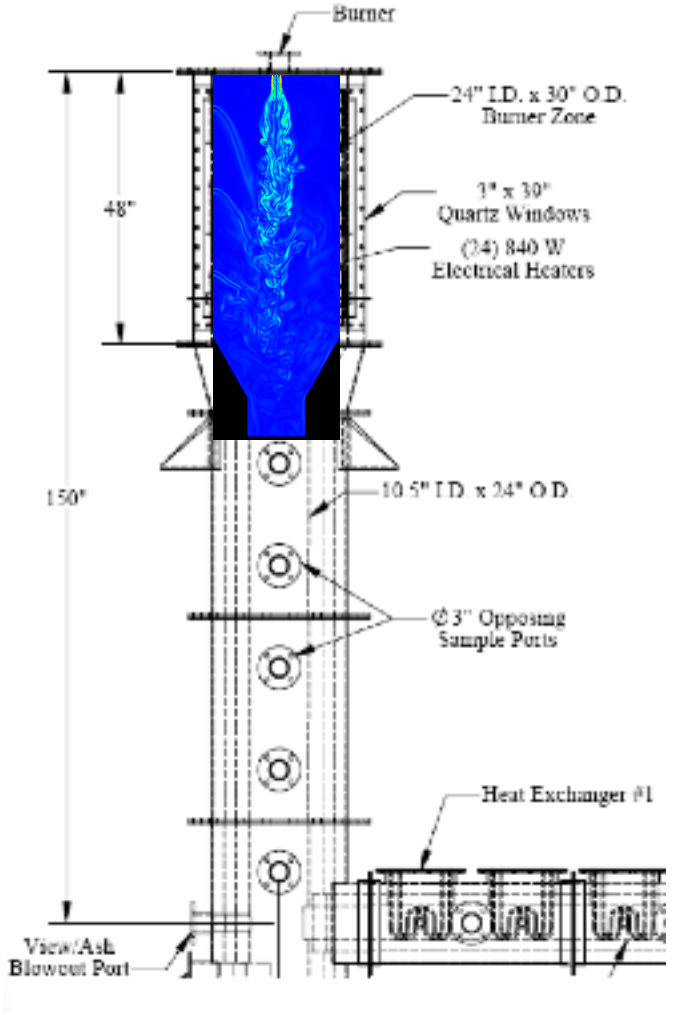
Sandia National Laboratories

Los Alamos NATIONAL LABORATORY EST. 1943

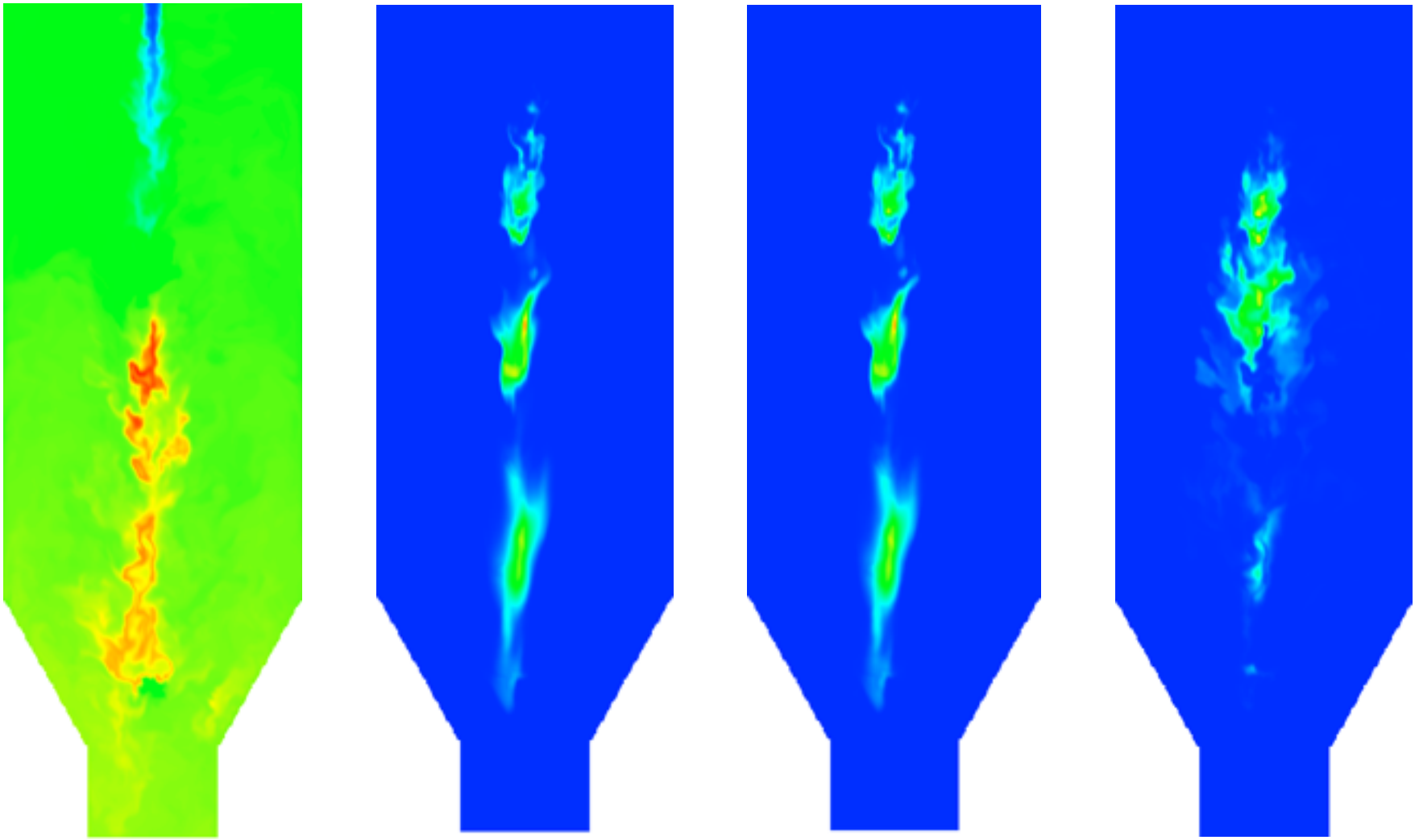
Thank You

OFC Validation—Experiments

- Stimpson et al. Proc. Comb. Inst. 34:2885-2893 (2013)
- Oxy-coal combustion
- Utah Skyline high-vol Bituminous coal
- 36 kW firing rate
- Two-color laser extinction soot measurements (line-of-sight)
- Rich S.R. = 0.9

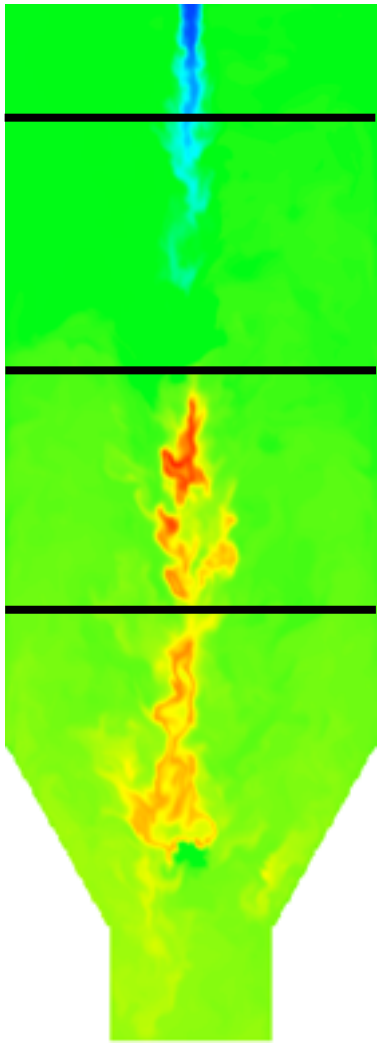


OFC Validation—Experiments

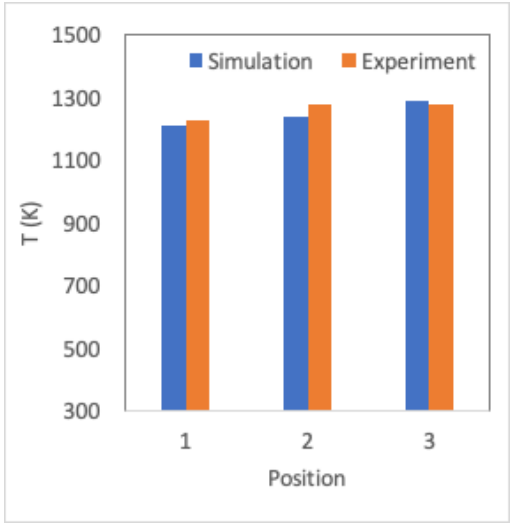


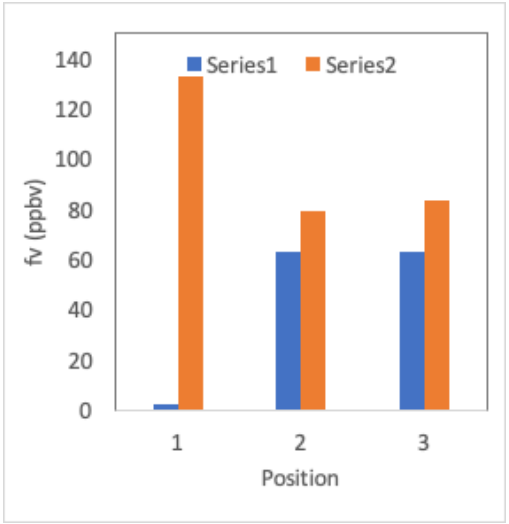
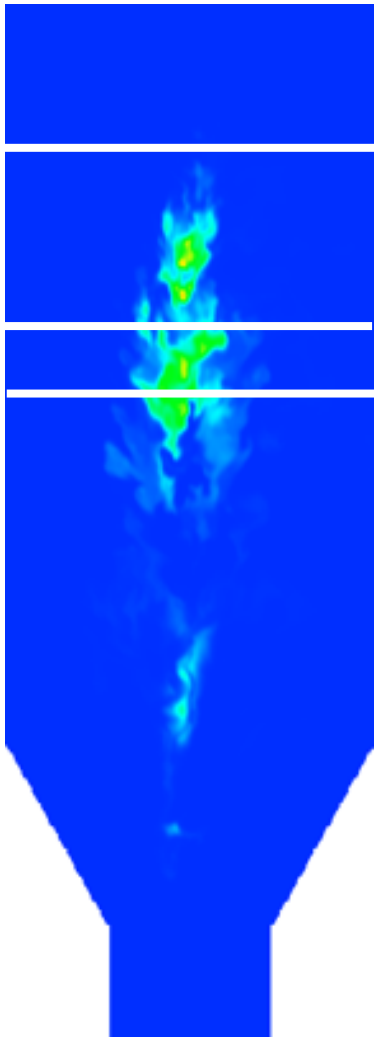
OFC Validation—Experiments

Temperature



	Temperature (K)			Soot fv (ppv)	
	Simulation	Experiment		Simulation	Experiment
Pos 1	1208	1225	**Pos 1**	2	133
Pos 2	1236	1275	**Pos 2**	63	79
Pos 3	1285	1275	**Pos 3**	63	83

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